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Organic ligand complexation at mineral surfaces studied via multiple internal reflection spectroscopy

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The interactions of a suite of naturally occurring simple carboxylic acids (undecenoic, oxalic, benzoic, phthalic and salicylic) with fluorite have been studied using IR spectroscopy, potentiometric titration, and batch slurry adsorption. Fluorite has been used as it is IR transparent and Ca is a key metal ion center on natural mineral surfaces; the acids have been chosen as they are useful proxies for humics and fulvics. Solution pH's between 3 and 8 were used to study the influence of pH on sorption mechanism.

Due to the difficulties of directly studying organic sorption to mineral surfaces a novel approach using multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIR) has been employed. With this arrangement the organics are sorbed directly on to the internal reflection element either eliminating the fluid phase or using a cell for in-situ measurements. Diagnostic shifts in peaks between solution and sorbed spectra are used in helping to determine the type of bonding between the ligands and a central metal ion. Spectra obtained from this method for phthalic acid in solution and adsorbed onto fluorite are displayed in figure 1.

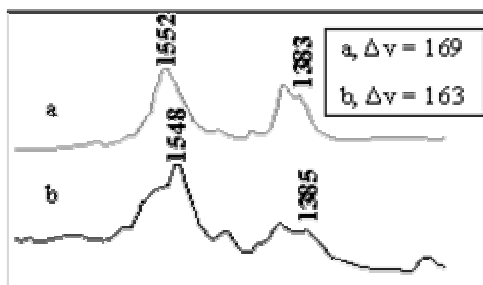


Fig 1. MIR-FTIR spectra of phthalate, (a) 0.1 μ M in solution at pH 3.8 (b) and complex formed at the CaF₂ surface.

The $\Delta\nu$ value is similar to those published for phthalic acid adsorbed on to simple metal oxides where the ligand has been proposed to coordinate through a bridging mode. All the acids sorbed onto fluorite show various modes of complexation.

In combination with the direct measurements, potentiometric titrations have been used to measure the dissolution rate, zero point of charge for fluorite, and adsorption isotherms of the acids established. The dissolution rate of CaF₂ at pH 3 is 4.16 x 10⁻¹⁴ moles cm⁻² s⁻¹. UV/visible spectroscopy and TOC were used to constrain sorption density via batch slurry experiments.

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Cation- π bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to hydrated mineral surfaces

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Sorption of organic molecules to soils and sediments is generally assumed to be controlled by sorption to natural organic matter, with important contributions of sorption to mineral surfaces if the organic molecules contain polar or ionic functional groups that form partial covalent or charge-transfer bonds with surface functional groups [1]. The contributions of weaker, noncovalent interactions to the sorption of nonionic organic compounds, such as polycyclic aromatic hydrocarbons, to hydrated mineral surfaces are not yet fully understood because of limited direct spectroscopic characterization. We have characterized the interactions of deuterium-labeled aromatic molecules with hydrated mineral surfaces using deuterium nuclear magnetic resonance (²H NMR) spectroscopy. Relaxation of the quadrupolar deuterium nuclei is related to the molecular correlation time (τ_c), thereby providing direct characterization of the molecular environments of adsorbed molecules [2]. Both ²H NMR and batch sorption experiments showed that softer exchangeable cations generally resulted in more sorption to the same mineral surfaces (e.g., Ag⁺ > Cs⁺ > Na⁺ > Mg²⁺, Ba²⁺), consistent with the sequence of cation- π_i electron binding energies in aqueous solution. In addition, aromatic organic sorption was dependent on the surface charge density of the minerals (e.g., vermiculite > silica gels > kaolinite). These results strongly suggest that cation- π_i bonding forms between PAHs and exchangeable cations at mineral surfaces and significantly affects PAH sorption to hydrated mineral surfaces [3-6].

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